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(54) Reinforced cellular polyester resin sheets

(57) Flat or shaped covering sheets are essentially constituted of a low density cellular material reinforced with glass fibers, based on unsaturated polyester resins. The sheets are suitable for covering buildings and areas, and possess opaqueness, high thermal insulating capacity, resistance for long periods to atmospheric agents and high mechanical characteristics whereby they provide a walking surface. Processes for transforming foams based on unsaturated polyester resins into plane or shaped sheets, reinforced with glass fibers, and having a cellular structure are disclosed.

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SPECIFICATION

New application of polymeric foams and process for obtaining products

The present invention has as an object new low density cellular articles, obtained from foams based on unsaturated polyester resins.

More specifically, the present invention has as an object a new type of flat or shaped cover sheets, characterized by the fact that they are essentially constituted of low density cellular material based on unsaturated polyester resins and in that they posses opaqueness, high thermal insulating capacity, resistance for long periods to atmospheric agents and high mechanical characteristics whereby they provide a walking surface. The present invention further concerns processes for transforming foams based on unsaturated polyester resins into the aforecited articles.

Plane or shaped sheets both for covering buildings and areas and for covering the outer walls of buildings are known. Particularly severe requirements are established especially for the first kind of sheets. These presently comprise substantially three different types.

The first type is represented by zinc-coated steel sheets having a small thickness (1-2 mm). Said sheets have the advantage that their weight is low and that they are opaque, which characteristic is generally required for covering buildings. However they have the defect that their resistance to atmospheric agents is limited, by which they are easily corroded, and that they provide inadequate thermal insulation, whereby the spaces covered thereby suffer from high thermal excursions in the warmer and colder seasons. The property of furnishing a walking surface is also reduced, viz. a person which walks on such a roof causes deformations and damages to the metal sheet, unless high thicknesses are used, which however are not interesting because of the consequent high weight and cost.

The second type, commonly known under the trade name "Externit", is obtained from a mixture of cement and asbestos fiber. It has the advantage of a low cost even for high thicknesses (5-9 mm) which permit walking thereon. Further it is opaque and has thermal insulation characteristics better than those of the zinc-coated sheets, even though not to the extent desired for many uses. Flat and corrugated 'Externit" type sheets have however two serious drawbacks. The processing of asbestos fibers is dangerous because they tend to cause cancer and is presently subjected to serious limitations, if it not wholly prohibited, in many countries. Further they become brittle with time because of the corrosion caused therein by snow and frost, and therefore they lose the requisite of affording a walking surface.

A third type is produced from unsaturated polyester resins reinforced with glass fibers (fiberglass). It differs from the two preceding types because of its transparency, a property which is desired for instance in covering open areas (such as courtyards), and because of its very low weight due to a limited thickness (0.8-2 mm). While their resistance to atmospheric agents is very good, they however have the drawback that they do not afford a walking surface and have a low thermal insulation. On the other hand it is not possible to render such sheets opaque merely by adding to the unsaturated polyester resin an opacizing mineral charge or filler (opacifier), because the limited thicknesses which characterize these sheets do not permit to obtain an adequate opacizing effect, unless much greater sheet thicknesses ($\geq$ 5 mm) are used, which thicknesses would render said products uneconomical.

The problem to the solution of which the present invention is directed is that of providing covering sheets, preferably corrugated or anyway shaped, having the positive characteristics of the "Eternit" type sheets without its drawbacks, viz. without the danger of promoting cancer which is inherent in the processing of asbestos fibers, the tendency to become brittle under the action of atmospheric agents and the limited thermal insulation capability.

The Applicant has now surprisingly found that by using a low density cellular material based on a foam of unsaturated polyester resins reinforced with glass fibers, it is possible to obtain sheets, in particular corrugated or anyway shaped rigid sheets, which have a high insulation capacity and high opaqueness, resistance to atmospheric agents for long periods and high mechanical characteristics which may provide a safe walking surface.

An object of the present invention are therefore flat or shaped covering sheets which possess opaqueness, high thermal insulation capacity, long term resistance to atmospheric agents and high mechanical characteristics which may provide a safe walking surface, said sheets being reinforced with glass fibers, characterized by the fact that they are essentially constituted by low density cellular material based on unsaturated polyester resins.

According to the present invention unsaturated polyester resins reinforced with glass fibers in the form of low density foams are employed for the production of said sheets, which foams are transformed into sheets having a cellular structure with prevalently closed cells, on the same machineries which are normally used for the production of transparent sheets of the third type hereinbefore specified.

A further object of the present invention is therefore a process for the preparation of the aforesaid sheets characterized by the fact that a low density foam essentially constituted by an unsaturated polyester resin reinforced with glass fibers is transformed by means of suitable conventional methods and apparatus.

The opacizing effect may be obtained, in the sheets which are an object of the present invention, even without adding opacizing fillers (opacifiers), inasmuch as their cellular structure in itself produces a high opaqueness. Further the sheets having cellular structure thus obtained have far superior characteristics of rigidity and therefore of providing a walking surface when compared with compact fiberglass sheets of like

thickness, even through their weight is the same or lower.

The density of the cellular structure of the sheets which are an object of the present invention, including the glass fibers and any filler which may be present, is preferably comprised between 0.3 and 0.9 kg/lt, more preferably between 0.5 and 0.8 kg/lt.

When compared with corrugated conventional glass fiber reinforced polyester (fiberglass) sheets having a density of about 1.4 kg/lt and a thickness of about 1.5 mm, the sheets which are an object of the present invention, which have a density e.g. of 0.64 kg/lt, have a thickness of 3.3 mm the weight being the same. Such a thickness of cellular material confers not only high opaqueness but also high rigidity, and this, at equal weight and raw materials cost of the two types of corrugated sheets which are here compared.

A comparison of the thermal insulating capacity of the two types of sheets considered provides, the weight being equal, the following experimental values: thermal conductivity of a conventional compact glass fiber reinforced polyester sheet, having a thickness of 1.5 mm:

$$Q = 113\ \mathrm{kcal/m^2h^\circ C}$$

thermal conductivity of a sheet of cellular material according to the present invention, having a density of 0.64 kg/lt and a thickness of 3.3 mm:

$$Q = 9\ \mathrm{kcal/m^2h^\circ C}$$

The sheets according to the present invention assure therefore in this case a thermal insulating capacity which is about 12 times higher than that of a conventional solid glass fiber reinforced polyester sheet. This without taking into account the heat transmitted by direct solar radiation, which in the case of glass fiber reinforced polyester resin is high because of its transparency while it is practically zero in the case of the opaque sheets of the present invention.

The sheets according to the present invention may also be covered on the side which is exposed to sunlight, with metal films or metal coated plastic films, which confer to the sheets high reflecting power, in order further to increase their thermal insulating capacity. As a metal for the coating, aluminium may be employed, preferably anodized aluminium.

The same effect may be obtained by dispersing in the foamed material with which the sheets of the present invention are produced, metal pigments in the form of powders of metals, such as e.g. aluminium. The sheets may also be suitable colored, e.g. by dispersing or dissolving pigments or dyes in the resins.

Any unsaturated polyester resin normally used for producing corrugated solid fiberglass sheets or the unsaturated polyester resins normally used for the production of laminates may be used for the production of sheets which are an object of the present invention. If, because of particular requirements, the sheets have to be self-extinguishing, this may be achieved in various ways, e.g. by adding to the unsaturated polyester resins a mineral filler which notoriously confers self-extinguishing properties to it, such as e.g. alumina hydrate in an amount higher than 10% by weight with respect to the resin, or by using a brominated or halogenated resin containing more than 5% by weight of halogen, the highest amount of alumina hydrate or halogen to be used depending on the degree of the self-extinguishing properties which it is desired to obtain.

For reinforcing the sheets of the present invention, commercial glass fibers are employed, preferably of the type called cut filaments mat, or of the type called continuous filaments mat, and/or of the type called chopped strand, oriented filaments; it is also possible to employ the glass fibers in the form of a woven roving or a fabric. The amount of glass fibers may be as high as 40% by weight of the composite used.

The process for producing the sheets of the present invention may employ continuous or discontinuous processing machinery used for producing laminates or stratified products of compact unsaturated polyester resin. The machineries used for producing the corrugated fiberglass sheets of the market in continuous operation may be used for the production of corrugated sheets from foamed material, which are one of the preferred objects of the present invention.

In the case of the sheets of foamed material of the present invention it is however necessary to carry out a foam production stage before the sheet production stage. Mechanical gas occlusion processes or physical or chemical expansion processes may be used for the production of the foam. The density of the foam, without taking into account the reinforcing glass fibers and any fillers that may be present, is generally comprised between 0.25 and 0.8 kg/lt, preferably between 0.4 and 0.7 kg/lt, and it should take into account, in calculating the desired density in the product, the increase of density due to the shrinkage of the resin during its successive hardening and to the greater density of the glass fibers and of the fillers which may be present.

The preferred process for the production of the foams is the mechanical occlusion of gas, in the form of prevalently closed bubbles, into an unsaturated polyester resin. Said process is described in detail in copending Italian Patent Application No. 22578 A/79, published in the Federal Republic of Germany as D.O.S. No. 30 16 333. Air or preferably an inert gas, such as nitrogen or carbon dioxide, is used as gas to be occluded.

As it has been said, the foam may also be produced, partly or completely, by physical or chemical expansion. Thus, e.g, the mechanical occlusion of gas may be substituted in whole or in part by physical expansion, by means of low boiling agents which evaporate thereby creating bubbles. Agents well known in

the art, such as n-pentane or fluorinated hydrocarbons, are used for this purpose. If chemical expansion is used, chemical reactions are employed which evolve gaseous compounds, such as for instance the decomposition of carbonates and bicarbonates or the reaction with isocyanates, reactions which are well known in the art.

In the case of physical or chemical expansion, contrary to what occurs in the mechanical occlusion of gas, the foam may be produced either previously or directly on the sheet production machine. If the foam is previously produced, as in the case of the mechanical occlusion of gas, it is necessary that the foam be stable and shall not collapse for a time sufficient to permit the production of the sheets. To that end it is necessary to incorporate into the foam stabilizing agents, as described in the aforecited Patent Application.

As to the incorporation of the glass fibers, two different systems may be adopted. If the foam is produced by mechanical occlusion of gas and the glass fibers called chopped strand are used, the fibers are preferably previously incorporated during the processing in the foam producing device, as described in the aforecited Patent Application.

If oriented filaments are used, these are predisposed on the laminating machine. If glass fibers in the form of cut filament mat or continuous filament mat are employed, it is preferable to immerse the mat, having a weight from 0.05 to 0.35 kg/m^2 per mm of sheet thickness, during the sheet lamination process, into the preformed foam or into the resin containing the physical or chemical expanding agent.

The second stage of the production of expanded material sheets, in particular corrugated or anyway shaped sheets, consists in laminating the foam containg the glass fibers and hardening it under such conditions as not to cause the foam to collapse, by using conventional continuous cycle machines, in particular machines for the production of compact corrugated fiberglass sheets. It is surprising that it is possible to use for said second stage conventional continuous cycle machines, if one considers the higher thicknesses of the sheets which must be produced from foamed material, the hardening cycle which is substantially different from that used for conventional compact fiberglass sheets, and finally the danger of foam collapse due to the temperatures reached during the hardening process.

The hardening of the foam containing the glass fibers occurs through the action of conventional cross-linking agents based on organic peroxides. Cross-linking systems are preferred which comprises acetylacetone- and/or cyclohexanone- and/or methylethylketone-peroxides, in combination with cobalt compounds, such as cobalt octoate, as accelerator. The amounts of peroxide and accelerator must be suitably controlled so as to obtain hardening times adequate to the dimensions and the speed of the machine which produces the sheets and with the stability of the foam.

The hardening temperature varies in general between room temperature and 100°C. It is preferable to change the temperature along the processing line so as to optimize the conditions which guarantee the hereinbefore specified requirements. As an example, it is convenient to use, for a machine for the production of corrugated sheets having a length of 50 m and a processing speed of 5 m per minute and a temperature of the hardening oven (having a length of 30 m) of 60-80°C, the following dosage of the cross-linking system: hydroquinone inhibitor = 250-350 ppm, cobalt octoate accelerator, as 6% by weight solution in styrene = 0.15-0.25% by weight, acetylacetone peroxide initiator = 0.5-1% by weight.

Both the foam production process and the sheet hardening process should be conducted in such a way as to obtain a cellular material containing mostly closed cells. This is necessary to provide sheets having good characteristics of thermal insulation and impermeability to atmospheric agents. For said reasons it is necessary that the closed cells constitute at least 70%, preferably at least 80%, of the total of the cells which are present. This may be obtained on the one hand by maintaining the foam production conditions described e.g. in the aforesaid Patent Application and, on the other hand, by observing the hardening conditions hereinbefore set forth.

The following examples have the purpose of illustrating the present invention without having a limitative character.

Example 1

An unsaturated polyester resin is prepared by polycondensation for 12 hours at about 190°C of:
- 2000 mols of maleic anhydride,
- 1000 mols of phthalic anhydride,
- 3100 mols of propylene-glycol.

After an acid number corresponding to 30 mg of KOH per 1 g of unsaturated polyester has been reached, the product is allowed to cool down to 110°C and then 223 kg of styrene, 250 g of hydroquinone and 1.5 kg of a 6% by weight solution of cobalt octoate in styrene, are added under good stirring. The resin thus obtained has a viscosity of 1300 centipoise at 25°C.

By using the resin thus obtained, a foam is continuously produced having a density of 0.5 kg/lt by mechanical occlusion of nitrogen according to the process described in Italian Patent Application No. 22579 A/79, published in the Federal Republic of Germany as D.O.S. No. 30 16 334.

By means of a dosing pump, 0.7% by weight of acetyl acetone peroxide is continuously fed to the foam thus obtained, immediately before it leaves the foaming machine.

Example 2

The foam produced according to Example 1 is used to feed a commercial machine for the continuous

production of fiberglass sheets. A flat sheet is produced having a thickness of 3.7 mm and a width of 1.35 m with a processing speed of 5 m/min. For this purpose the foam is fed to the sheet producing machine at a speed of 827 kg/h. The foam is uniformly distributed on the conveyor belt of the machine, and simultaneously a continuous glass filament mat having width of 1.35 m and a weight of 375 g/m^2 is immersed into the foam. The body thus formed is laminated and passes thereafter through an oven heated to 70°C, having a length of 30 m. At the oven outlet the sheet is perfectly hardened and is thereafter cut and removed.

Characteristic properties of the sheet produced:

Density	= 0.58 kg/lt
Glass fiber content	= 18% by weight
Tensile strength	= 140 kg/cm^2
Tensile modulus	= 17100 kg/cm^2
Thickness	= 3.7 mm
Transparency to sunlight	= none

Example 3

A sheet having a thickness of 6 mm is obtained by using the foam produced according to Example 1 using a technique equal to that of Example 2. For this purpose the sheet producing machine is fed with 1341 kg/h of foam and with a continuous glass filament mat having a weight of 608 kg/m^2. The lamination, hardening and cutting cycle is the same as in Example 1.

Example 4

Corrugated sheets having thickness of 3.7 mm and a width of 1.054 m are continuously produced from the foam prepared according to Example 1 and with the technique and the amount of materials of Example 2. The foam is fed at a rate of 646 kg/h and the continuous glass filament mat having a width of 1.054 and a weight of 375 g/m^2 is simultaneously fed. Contrary to Example 2, the foam layer embodying the glass filament mat is passed, after the lamination and before entering the oven, over patterns having the shape of a commercial "Externit" type corrugated sheet, whereafter it enters the oven and is cut at the outlet from the oven.

The characteristics of the sheets obtained correspond to those of the sheets of Example 2.

Example 5

An unsaturated polyester resin is produced in the way described in Example 1, but using the following components:

- 550 mols of hexachloro-endomethylene- tethrahydrophthalic acid
- 450 mols of maleic anhydride
- 850 mols of diethylene glycol
- 250 mols of propylene glycol

The polycondensation is effected for 10 hours at 165°c until an acidity is reached corresponding to 30 mg of KOH per 1 g of unsaturated polyester. The product is then cooled down to 110°C and 200 kg of styrene, 160 g of toluhydroquinone and 1.06 kg of a 6% by weight solution of cobalt octoate in styrene are added to the 335 kg of polyester thus obtained.

543 kg of resin thus obtained are mixed with 534 kg of the resin obtained according to Example 1. Said resin mixture is used for continuously producing a foam having a density of 0.5 kg, by mechanical occlusion of nitrogen according to the process described in Italian Patent Application No. 22578 A/79, published in the Federal Republic of Germany as D.O.S. No. 30 16 333.

By means of a dosing pump, 1% by weight of acetyl acetone peroxide is continuously fed to the foam thus obtained, immediately before it leaves the foaming machine.

Example 6

The foam produced according to Example 5 is used to feed a commercial machine for the continuous production of resin-fiberglass sheets. A flat sheet is produced having a thickness of 3.7 mm and a width of 1.35 m with a processing speed of 5 m/min. For this purpose the foam is fed on the sheet producing machine at a rate of 895 kg/h. The foam is uniformly distributed on the conveyor belt of the machine and simultaneously a continuous glass filament mat having a width of 1.35 m and a weight of 375 g/m^2 is immersed into the foam. The body thud formed is laminated and passes thereafter through an oven heated to 70°C, having a length of 30 m. At the outlet from the oven the sheet is perfectly hardened and is thereafter cut and removed.

Characteristic properties of the sheet:

Density	= 0.62 kg/lt
Glass fiber content	= 17.5% by weight
Tensile strength	= 132 kg/cm^2
Tensile modulus	= 18200 kg/cm^2
Thickness	= 3.7 mm
Transparency to sunlight	= none

The sheet is self-extinguishing.

CLAIMS

1. Flat or shaped covering sheets having opaqueness, high thermal insulation capacity, resistance for long periods to atmospheric agents and high mechanical characteristics which may provide a safe walking surface, said sheets being characterized by the fact that they are essentially constituted of low density cellular material based on unsaturated polyester resins, said sheets being reinforced with glass fibers.
2. Covering sheets according to claim 1, characterized by the fact that they are rigid and flat.
3. Covering sheets according to claim 1, characterized by the fact that they are rigid and shaped.
4. Covering sheets according to claim 1,2 or 3, characterized by the fact that they contain other fillers.
5. Covering sheets according to any preceding claims, characterized in that the glass fibers are used in the form of continuous filament mat, cut filament mat and/or cut filaments called chopped strand and/or oriented filaments.
6. Covering sheets according to any preceding claims, characterized in that they have a density comprised between 0.3 and 0.9 kg/lt.
7. Covering sheets according to any preceding claim, characterized in that they have a density comprised 0.5 and 0.8 kg/lt.
8. Covering sheets according to any preceding claim, characterized in that they have over 70% of closed cells.
9. Covering sheets according to any preceding claim, characterized that they are self-extinguishing.
10. Covering sheets according to claim 9, characterized by the fact that they contain more than 10% by weight of alumina hydrate.
11. Covering sheets according to claim 9, characterized by the fact that they have been prepared from unsaturated polyester resin containing more than 5% of chemically bound bromine or other halogen.
12. Covering sheets according to any preceding claim, characterized in that they are coated with metal films or metal coated plastic films.
13. Covering sheets according to claim 12, characterized by the fact that anodized aluminium is used for the metal coating.
14. Covering sheets according to any one of claims 1 - 11, characterized in that they contain metal pigments in the form of metal powders.
15. Covering sheets according to any one of claims 1 - 11 characterized in that they are coloured by means of pigments or dyes.
16. Process for obtaining the covering sheets according to any preceding claim characterized in that a foam based on an unsaturated polyester resin is used.
17. Process according to claim 16, characterized by the fact that the foam has a density comprised between 0.25 and 0.8 kg/lt.
18. Process according to claim 16 or 17 characterized by the fact that the foam has a density comprised between 0.4 and 0.7 kg/lt.
19. Process according to claim 16, 17 or 18 characterized by the fact that the foam is obtained by mechanical occlusion of gas.
20. Process according to claim 19, characterized by the fact that the occluded gas is an inert gas chosen among nitrogen and/or carbon anhydride.
21. Process according to any one of claims 16 - 20, characterized in that the foam is produced by means . of a physical expanding agent.
22. Process according to any one of claims 16 - 20, characterized in that the foam is produced by means of a physical expanding agent.
22. Process according to any one of claims 16 - 20, characterized in that the foam is produced by chemical
23. Process according to any one of claims 16-22 characterized in that the foam is hardened in a machine for the production of plane or profiled sheets by means of initiators based on organic peroxides.
24. Process according to claim 23, characterized by the fact that the initiators based on organic peroxides are used together with an accelerator constituted by a cobalt compound.
25. Process according to claim 23 or 24 characterized by the fact that the hardening of the foam takes

place at a temperature between room temperature and 100°C.

26. Process according to claim 23,24 or 25, characterized by the fact that the hardening of the foam takes place in a continuous process, by immersing a continuous glass filament mat into a foam and passing the body thus obtained through machinery comprising a laminating machine, a hardening oven, and a system for cutting the hardened sheets.

27. Process according to any one of claims 23 - 26, characterized in that a device comprising patterns having the shape of a corrugated sheet is inserted between the laminating machine and the hardening oven.

28. Covering sheets obtained according to a process claimed in any one of claims 23 - 27.

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